PROCESS FOR THE HYDROFORMYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS

The present invention relates to the hydroformylation of ethylenically unsaturated compounds by reaction with carbon monoxide and hydrogen in the presence of a catalyst system.

The carbonylation and hydroformylation of ethylenically unsaturated compounds using carbon monoxide in the presence of hydrogen and a catalyst comprising a group VIII metal, example, rhodium, and a phosphine ligand, example an alkyl phosphine, cycloalkyl phosphine, aryl phosphine, pyridyl phosphine or bidentate phosphine, has been described in numerous patents and patent applications.

WO 96/19434 disclosed that a particular group of bidentate phosphine compounds can provide stable catalysts in carbonylation reaction systems, and the use of such catalysts leads to reaction rates which were significantly higher than those previously disclosed.

WO 01/68583 discloses carbonylation processes for higher alkenes of three or more carbon atoms.

WO 02/76996, for example, discloses a method for producing diphosphines, and their use as co-catalyst for hydroformylating olefins. WO 02/20448 similarly discloses the preparation of arylphosphines for the rhodium-catalysed hydroformylation of alkenes.

Although catalyst systems have been developed which exhibit reasonable stability during the hydroformylation process and permit relatively high reaction rates and regioselectivity between linear and branched aldehyde products, there still exists a need for alternative and/or improved catalyst systems. Suitably, the present invention aims to provide an alternative and/or improved catalyst for hydroformylating ethylenically unsaturated compounds. Moreover, the present invention aims to provide solvents which improve the performance of the catalyst system.

Surprisingly, it has been found that improved selectivity of the linear aldehyde product compared to the branched aldehyde product can be obtained than by using comparative catalyst systems of the prior art.

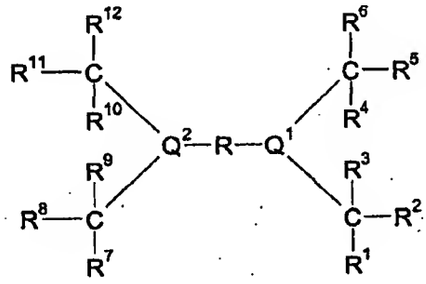
According to the present invention there is provided a process for the hydroformylation of ethylenically unsaturated compounds, as set forth in the appended claims. Preferred features of the invention will be apparent from the dependent claims, and the description. Also according to the present invention there is provided a catalyst system, a hydroformylation reaction catalyst system, a reaction medium, a hydroformylation reaction medium, use of a catalyst system, use of a reaction medium, and a process for preparing a catalyst system and reaction medium, as set forth hereinafter and in the appended claims.

According to the first aspect of the present invention there is provided a process for the hydroformylation of ethylenically unsaturated compounds, which process

comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of a catalyst system and a solvent, the catalyst system obtainable by combining:

a) a metal of Group VIII or a compound thereof; and
b) a bidentate phosphine of general formula (Ia)

(Ia)



wherein R is a covalent bridging group;

R^1 to R^{12} each independently represent hydrogen, lower alkyl, aryl or Het, preferably, lower alkyl, aryl or Het;

Q^1 and Q^2 each independently represent phosphorus, arsenic or antimony and in the latter two cases references to phosphine or phosphorus above are amended accordingly,

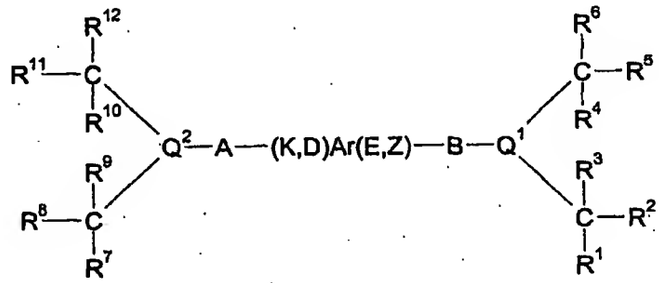
the process characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent.

Such a process is referred to hereinafter as "the process of the invention". The process of the invention includes the embodiments set out hereinafter.

In one set of embodiments, the group R in formula (Ia) may represent an alkylene bridging group, preferably, a lower alkylene.

In another and preferred set of embodiments, the bridging group R may be defined as -A-(K,D)Ar(E,Z)-B-, such that general formula (Ia) becomes general formula (I),

(I)



wherein:

Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$, or -J-$Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro,

OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$;

R^1 to R^{18} each independently represent hydrogen, lower alkyl, aryl, or Het, preferably, lower alkyl, aryl or Het;

R^{19} to R^{27} each independently represent hydrogen, lower alkyl, aryl or Het;

Q^1, Q^2 and Q^3 (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly.

Preferably, when K, D, E or Z represent -J-$Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, the respective K, D, E or Z is on the aryl carbon adjacent the aryl carbon to which A or B is connected or, if not so adjacent, is adjacent a remaining K, D, E or Z group which itself represents -J-$Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$.

Preferably, R^1 to R^{18} each independently represent lower alkyl or aryl. More preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, C_1-C_6 alkyl phenyl (wherein the phenyl group is optionally substituted as defined herein) or phenyl (wherein the phenyl group is optionally substituted as defined herein). Even more preferably, R^1 to R^{18} each independently represent C_1 to C_6 alkyl, which is optionally substituted as defined herein. Most preferably, R^1 to R^{18} each represent non-substituted C_1 to C_6 alkyl such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl.

Alternatively, or additionally, each of the groups R^1 to R^3, R^4 to R^6, R^7 to R^9, R^{10} to R^{12}, R^{13} to R^{15} or R^{16} to R^{18} together independently may form cyclic structures such as 1-norbornyl or 1-norbornadienyl. Further examples of composite groups include cyclic structures formed between R^1 to R^6, R^7 to R^{12}, and R^{13} to R^{18}. Alternatively, one or more of the groups may represent a solid phase to which the ligand is attached.

Moreover, at least one ($CR^xR^yR^z$) group attached to Q^1 and/or Q^2, i.e. $CR^1R^2R^3$, $CR^4R^5R^6$, $CR^7R^8R^9$, or $CR^{10}R^{11}R^{12}$, may instead be congressyl or adamantyl, or both groups defined above as ($CR^xR^yR^z$) attached to either or both Q^1 and/or Q^2, may, together with either Q^1 or Q^2 as appropriate, instead form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof. However, in this particular set of embodiments, i.e. when the bridging group is defined as -A-(K,D)Ar(E,Z)-, if any ($CR^xR^yR^z$) groups are defined as per this paragraph, they are preferably congressyl or adamantyl, more preferably non-substituted adamantyl or congressyl, most preferably a non-substituted adamantyl group.

In a particularly preferred embodiment of the present invention R^1, R^4, R^7, R^{10}, R^{13} and R^{16} each represent the same lower alkyl, aryl or Het moiety as defined herein, R^2, R^5, R^8, R^{11}, R^{14} and R^{17} each represent the same lower alkyl, aryl or Het moiety as defined herein, and R^3, R^6, R^9, R^{12}, R^{15} and R^{18} each independently represent the same lower alkyl, aryl or Het moiety as defined herein. More preferably R^1, R^4, R^7, R^{10}, R^{13} and R^{16} each independently represent the same C_1-C_6 alkyl, particularly non-

substituted C_1-C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl or cyclohexyl; R^2, R^5, R^8, R^{11}, R^{14} and R^{17} each independently represent the same C_1-C_6 alkyl as defined above; and R^3, R^6, R^9, R^{12}, R^{15} and R^{18} each independently represent the same C_1-C_6 alkyl as defined above. For example: R^1, R^4, R^7, R^{10}, R^{13} and R^{16} each represent methyl; R^2, R^5, R^8, R^{11}, R^{14} and R^{17} each represent ethyl; and, R^3, R^6, R^9, R^{12}, R^{15} and R^{18} each represent n-butyl or n-pentyl.

In an especially preferred embodiment of the present invention each R^1 to R^{18} group represents the same lower alkyl, aryl, or Het moiety as defined herein. Preferably, each R^1 to R^{18} represents the same C_1 to C_6 alkyl group, particularly non-substituted C_1-C_6 alkyl, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl and cyclohexyl. Most preferably, each R^1 to R^{18} represents methyl.

In the compound of formula (I), preferably each Q^1, Q^2 and Q^3 (when present) is the same. Moreover, in a compound of formula (Ia), preferably Q^1 and Q^2 are the same. Most preferably, each Q^1, Q^2 and Q^3 (when present) represents phosphorous.

Preferably, in the compound of formula (I), A, B and J (when present) each independently represent C_1 to C_6 alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Moreover, in the compound of formula (Ia), R (when alkylene) represents C_1 to C_6 alkylene which is optionally substituted as defined herein, for example with lower alkyl groups. Preferably, the lower alkylene groups which A, B and J

(when present) represent are non-substituted. A particular preferred lower alkylene which A, B and J may independently represent is $-CH_2-$ or $-C_2H_4-$. Most preferably, each of A, B and J (when present) represent the same lower alkylene as defined herein, particularly $-CH_2-$. Particularly preferred lower alkylenes which R represents are substituted or non-substituted and may be selected from ethylene ($-C_2H_4-$), and substituted variants thereof, propylene ($-C_4H_6-$), and substituted variants thereof, and butylene ($-C_4H_8-$), and substituted variants thereof, and wherein such substitution may be on any, some or all of the carbon atoms of the lower alkylene and such substitution may be with lower alkyl groups. More preferably, the lower alkylenes which R represents are substituted or non-substituted ethylene or propylene, most preferably, substituted or non-substituted propylene.

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, K, D, E or Z represents hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E or Z represent hydrogen, phenyl, C_1-C_6 alkylphenyl or C_1-C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Most preferably, K, D, E or Z represents hydrogen.

Preferably, in the compound of formula (I) when K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, K, D, E and Z each independently represent hydrogen, lower alkyl, phenyl or lower alkylphenyl. More preferably, K, D, E and Z each independently represent hydrogen, phenyl, C_1-C_6 alkylphenyl or C_1-C_6 alkyl, such as methyl, ethyl, propyl, butyl, pentyl and hexyl. Even more preferably, K, D, E and

Z represent the same substituent. Most preferably, they represent hydrogen.

Preferably, in the compound of formula (I) when K, D, E or Z does not represent $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached do not form a phenyl ring, each of K, D, E and Z represent the same group selected from hydrogen, lower alkyl, aryl, or Het as defined herein; particularly hydrogen or C_1-C_6 alkyl (more particularly unsubstituted C_1-C_6 alkyl), especially hydrogen.

Preferably, in the compound of formula (I) when two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring, then the phenyl ring is optionally substituted with one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined herein). More preferably, the phenyl ring is not substituted by any substituents i.e. it bears hydrogen atoms only.

Preferred compounds of formula (I) within this set of embodiments include those wherein:

A and B each independently represent unsubstituted C_1 to C_6 alkylene;

K, D, Z and E each independently represent hydrogen, C_1-C_6 alkyl, phenyl, C_1-C_6 alkylphenyl or -J-$Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J represents unsubstituted C_1 to C_6 alkylene; or two of K, D, Z and E together with the carbon atoms of the aryl ring to which they are attached form a phenyl ring which is optionally substituted by one or more substituents selected from lower alkyl, phenyl or lower alkylphenyl.

R^1 to R^{18} each independently represent C_1 to C_6 alkyl, phenyl or C_1 to C_6 alkylphenyl.

Further preferred compounds of formula (I) within this set of embodiments include those wherein:

A and B both represent $-CH_2-$ or C_2H_4, particularly CH_2;

K, D, Z and E each independently represent hydrogen, C_1-C_6 alkyl phenyl or C_1-C_6 alkyl or -J-$Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ where J is the same as A; or two of K, D, E and Z together with the carbon atoms of the aryl ring to which they are attached form an unsubstituted phenyl ring;

R^1 to R^{18} each independently represent C_1 to C_6 alkyl;

Still further preferred compounds of formula (I) within this set of embodiments include those wherein:

R^1 to R^{18} are the same and each represents C_1 to C_6 alkyl, particularly methyl.

Still further preferred compounds of formula I within this set of embodiments include those wherein:

K, D, Z and E are each independently selected from the group consisting of hydrogen or C_1 to C_6 alkyl, particularly where each of K, D, Z and E represent the same group, especially where each of K, D, Z and E represent hydrogen; or

K represents $-CH_2-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and D, Z and E are each independently selected from the group consisting of hydrogen or C_1 to C_6 alkyl, particularly where both D and E represent the same group, especially where D, Z and E represent hydrogen.

Especially preferred specific compounds of formula (I) within this set of embodiments include those wherein:

each R^1 to R^{12} is the same and represents methyl;
A and B are the same and represent $-CH_2-$;
K, D, Z and E are the same and represent hydrogen.

In this particular set of embodiments, Ar may be defined as are "Ar" and "aryl" hereinafter, but preferably, Ar is defined as including six-to-ten-membered carbocyclic aromatic groups, such as phenyl and naphthyl, which groups are optionally substituted with, in addition to K, D, E or Z, one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl

(which alkyl group may itself be optionally substituted or terminated as defined hereinafter).

In a further set of embodiments, in a compound of either formula (I) or (Ia) at least one ($CR^xR^yR^z$) group attached to Q^1 and/or Q^2, i.e. $CR^1R^2R^3$, $CR^4R^5R^6$, $CR^7R^8R^9$, or $CR^{10}R^{11}R^{12}$, may instead be congressyl or adamantyl, or both groups defined above as ($CR^xR^yR^z$) attached to either or both Q^1 and/or Q^2, may, together with either Q^1 or Q^2 as appropriate, instead form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, preferably the at least one ($CR^xR^yR^z$) group being congressyl or adamantyl.

The adamantyl group may optionally comprise, besides hydrogen atoms, one or more substituents selected from lower alkyl, $-OR^{19}$, $-OC(O)R^{20}$, halo, nitro, $-C(O)R^{21}$, $-C(O)OR^{22}$, cyano, aryl, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-CF_3$, $-P(R^{56})R^{57}$, $-PO(R^{58})(R^{59})$, $-PO_3H_2$, $-PO(OR^{60})(OR^{61})$, or $-SO_3R^{62}$, wherein R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28} (defined as are R^{19} to R^{27} hereinbefore), lower alkyl, cyano and aryl are as defined herein and R^{56} to R^{62} each independently represent hydrogen, lower alkyl, aryl or Het. However, in one embodiment, the adamantyl groups are not substituted.

Suitably, when the adamantyl group is substituted with one or more substituents as defined above, highly preferred substituents include unsubstituted C_1 to C_8 alkyl, $-OR^{19}$, $-OC(O)R^{20}$, phenyl, $-C(O)OR^{22}$, fluoro, $-SO_3H$, $-N(R^{23})R^{24}$, $-P(R^{56})R^{57}$, $-C(O)N(R^{25})R^{26}$ and $-PO(R^{58})(R^{59})$, $-CF_3$, wherein R^{19} represents hydrogen, unsubstituted C_1-C_8 alkyl or phenyl, R^{20}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26} each independently represent

hydrogen or unsubstituted C_1-C_8 alkyl, R^{56} to R^{59} each independently represent unsubstituted C_1-C_8 alkyl or phenyl.

Suitably, the adamantyl group may comprise, besides hydrogen atoms, up to 10 substituents as defined above, preferably up to 5 substituents as defined above, more preferably up to 3 substituents as defined above. Suitably, when the adamantyl group comprises, besides hydrogen atoms, one or more substituents as defined herein, preferably each substituent is identical. Preferred substituents are unsubstituted C_1-C_8 alkyl and trifluoromethyl, particularly unsubstituted C_1-C_8 alkyl such as methyl. A highly preferred adamantyl group comprises hydrogen atoms only i.e. the adamantyl group is not substituted.

Preferably, when more than one adamantyl group is present in a compound of formula (Ia) or (I), each adamantyl group is identical.

The 2-phospha-tricyclo[3.3.1.1.{3,7}]decyl group (referred to as 2-phospha-adamantyl group herein) may optionally comprise, beside hydrogen atoms, one or more substituents. Suitable substituents include those substituents as defined herein in respect of the adamantyl group. Highly preferred substituents include lower alkyl, particularly unsubstituted C_1-C_8 alkyl, especially methyl, trifluoromethyl, $-OR^{19}$ wherein R^{19} is as defined herein particularly unsubstituted C_1-C_8 alkyl or aryl, and 4-dodecylphenyl. When the 2-phospha-adamantyl group includes more than one substituent, preferably each substituent is identical.

Preferably, the 2-phospha-adamantyl group is substituted on one or more of the 1, 3, 5 or 7 positions with a substituent as defined herein. More preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3 and 5 positions. Suitably, such an arrangement means the phosphorous atom of the 2-phospha-adamantyl group is bonded to carbon atoms in the adamantyl skeleton having no hydrogen atoms. Most preferably, the 2-phospha-adamantyl group is substituted on each of the 1, 3, 5 and 7 positions. When the 2-phospha-adamantyl group includes more than 1 substituent preferably each substituent is identical. Especially preferred substituents are unsubstituted C_1-C_8 alkyl and trifluoromethyl, particularly unsubstituted C_1-C_8 alkyl such as methyl.

Preferably, 2-phospha-adamantyl represents unsubstituted 2-phospha-adamantyl or 2-phospha-adamantyl substituted with one or more unsubstituted C_1-C_8 alkyl substituents, or a combination thereof.

Preferably, the 2-phospha-adamantyl group includes additional heteroatoms, other than the 2-phosphorous atom, in the 2-phospha-adamantyl skeleton. Suitable additional heteroatoms include oxygen and sulphur atoms, especially oxygen atoms. More preferably, the 2-phospha-adamantyl group includes one or more additional heteroatoms in the 6, 9 and 10 positions. Even more preferably, the 2-phospha-adamantyl group includes an additional heteroatom in each of the 6, 9 and 10 positions. Most preferably, when the 2-phospha-adamantyl group includes two or more additional heteroatoms in the 2-phospha-adamantyl skeleton, each of the additional heteroatoms are

identical. An especially preferred 2-phospha-adamantyl group, which may optionally be substituted with one or more substituents as defined herein, includes an oxygen atom in each of the 6, 9 and 10 positions of the 2-phospha-adamantyl skeleton.

Preferably, the 2-phospha-adamantyl includes one or more oxygen atoms in the 2-phospha-adamantyl skeleton.

Highly preferred 2-phospha-adamantyl groups as defined herein include 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5-trimethyl-6,9,10-trioxadamantyl group, 2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxadamantyl group, and 2-phospha-1,3,5-tri(trifluoromethyl)-6,9,10-trioxadamantyl group. Most preferably, the 2-phospha-adamantyl is selected from 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group or 2-phospa-1,3,5,-trimethyl-6,9,10-trioxadamantyl group.

Preferably, when more than one 2-phospha-adamantyl group is present in a compound of formula (I) or (Ia), each 2-phospha-adamantyl group is identical.

The 2-phospha-adamantyl group may be prepared by methods well known to those skilled in the art. Suitably, certain 2-phospha-adamantyl compounds are obtainable from Cytec Canada Inc of 901 Garner Road, Niagara Falls, Ontario, Canada L2E 6T4. Likewise corresponding 2-phospha-adamantyl compounds of formula (I) etc may be prepared by analogous methods.

Moreover, at least one of $CR^{13}(R^{14})(R^{15})$ and $CR^{16}(R^{17})(R^{18})$, when present, may instead be congressyl or adamantyl, optionally substituted as described above, or both groups defined as $CR^{13}(R^{14})(R^{15})$ and $CR^{16}(R^{17})(R^{18})$ attached to Q^3, may together with Q^3, instead form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, preferably the at least one of $CR^{13}(R^{14})(R^{15})$ and $CR^{16}(R^{17})(R^{18})$, when present, being congressyl or adamantyl.

Preferably, in a compound of formula (I) when both K represents $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$ and E represents $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$, then D represents $-J-Q^3(CR^{13}(R^{14})(R^{15}))CR^{16}(R^{17})(R^{18})$.

By the term 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group we mean a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^1, together with Q^1 to which they are attached, a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^2, together with Q^2 to which they are attached, a 2-phospha-adamantyl group formed by the combination of the two groups attached to Q^3, together with Q^3 to which they are attached, wherein Q^1, Q^2, or Q^3 is in the 2-position of the adamantyl group of which it forms an integral part and each of Q^1, Q^2, and Q^3 represents phosphorus.

Preferred compounds within the present set of embodiments and wherein at least one 2-phospha-adamantyl group is present include those wherein:

Groups $CR^1(R^2)(R^3)$ and $CR^4(R^5)(R^6)$ are attached to Q^1, and the groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group;

Groups $CR^1(R^2)(R^3)$ and adamantyl are attached to Q^1, and the groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group;

Groups $CR^1(R^2)(R^3)$ and congressyl are attached to Q^1, and the groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group;

Two adamantyl groups are attached to Q^1, and the groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group;

Two congressyl groups are attached to Q^1, and the groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group;

The groups attached to Q^1, together with Q^1, form a 2-phospha-adamantyl group, and the two groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group.

Naturally, in the preferred compounds noted above, Q^1 and Q^2 can be interchanged, together with the groups attached thereto. Therefore, for example, the first preferred compound in the list could equally preferably be:

Groups $CR^7(R^8)(R^9)$ and $CR^{10}(R^{11})(R^{12})$ are attached to Q^2, and the groups attached to Q^1, together with Q^1, form a 2-phospha-adamantyl group.

Highly preferred compounds within this embodiment include those wherein:

The groups attached to Q^1, together with Q^1, form a 2-phospha-adamantyl group, and the two groups attached to Q^2, together with Q^2, form a 2-phospha-adamantyl group.

Preferably, the groups attached to Q^1 are identical.

Preferably, the groups attached to Q^1 are identical, the groups attached to Q^2 are identical, and the groups attached to Q^3 are identical, more preferably, all such groups are identical or form with the Q they are attached to, identical groups.

Particularly preferred combinations in the present invention include those of formula (I) wherein:

(1) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen;
Q^1 and Q^2 both represent phosphorus.

(2) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;

K represents $-CH_2-Q^3(X^5)X^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
Q^1, Q^2 and Q^3 each represent phosphorus;
D and E are the same and represent hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen.

(3) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
K represents $-CH_2-Q^3(X^5)X^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
Q^1, Q^2 and Q^3 each represent phosphorus.

In a further set of embodiments, in formula (I), Ar is a cyclopentadienyl group, and Z may be represented by $-M(L_1)_n(L_2)_m$ and Z is connected via a metal ligand bond to the cyclopentadienyl group, M represents a Group VIB or VIIIB metal or metal cation thereof; and
L_1 represents a cyclopentadienyl, indenyl or aryl group each of which groups are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$ or ferrocenyl;

L_2 represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

R^{43} to R^{48} each independently represent hydrogen, lower alkyl, aryl or Het;

n = 0 or 1;

and m = 0 to 5;

provided that when n = 1 then m equals 0, and when n equals 0 then m does not equal 0.

Preferably, A, B, Q^1, Q^2, K, D, E, and R^1 to R^{27} are as defined and described hereinbefore, including preferred embodiments thereof.

By the term "M represents a Group VIB or VIIIB metal" in a compound of formula I we include metals such as Cr, Mo, W, Fe, Co, Ni, Ru, Rh, Os, Ir, Pt and Pd. Preferably, the metals are selected from Cr, Mo, W, Fe, Co, Ni, Ru and Rh. For the avoidance of doubt, references to Group VIB or VIIIB metals herein should be taken to include Groups 6, 8, 9 and 10 in the modern periodic table nomenclature.

By the term "metal cation thereof" we mean that the Group VIB or VIIIB metal (M) in the compound of formula I as defined herein has a positive charge. Suitably, the metal cation may be in the form of a salt or may comprise weakly coordinated anions derived from halo, nitric acid; sulphuric acid; lower alkanoic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid,

fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; perfluororated carboxylic acid such as trichloroacetic acid and trifluoroacetic acid; orthophosphoric acid; phosphonic acid such as benzene phosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. Other sources which may provide suitable anions include the tetraphenyl borate derivatives.

Preferably M represents a Group VIB or VIIIB metal. In other words the total electron count for the metal M is 18.

Halo groups, which L_2 may represent and with which the above-mentioned groups may be substituted or terminated, include fluoro, chloro, bromo and iodo.

Suitably, if A represents cyclopentadienyl and n = 1, the compounds of formula I may contain either two cyclopentadienyl rings, two indenyl rings or one indenyl and one cyclopentadienyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "sandwich compounds" as the metal M or metal cation thereof is sandwiched by the two ring systems. The respective cyclopentadienyl and/or indenyl ring systems may be substantially coplanar with respect to each other or they may be tilted with respect to each other (commonly referred to as bent metallocenes).

Alternatively, when n = 1, the compounds of the invention may contain either one cyclopentadienyl or one indenyl ring (each of which ring systems may optionally be substituted as described herein) and one aryl ring (i.e. L_1 represents aryl) which is optionally substituted as defined herein. Suitably, when n = 1 and L_1 represents aryl then the metal M of the compounds of formula I as defined herein is typically in the form of the metal cation.

Suitably, when n = 0, the compounds of the invention contain only one cyclopentadienyl or indenyl ring (each of which ring systems may optionally be substituted as described herein). Such compounds may be referred to as "half sandwich compounds". Preferably, when n = 0 then m represents 1 to 5 so that the metal M of the compounds of formula I has an 18 electron count. In other words, when metal M of the compounds of formula I is iron, the total number of electrons contributed by the ligands L_2 is typically five.

Suitably, the metal M or metal cation thereof in the cyclopentadienyl compounds of formula I is typically bonded to the cyclopentadienyl ring(s) or the cyclopentadienyl moiety of the indenyl ring(s). Typically, the cyclopentadienyl ring or the cyclopentadienyl moiety of the indenyl ring exhibits a pentahapto bonding mode with the metal; however other bonding modes between the cyclopentadienyl ring or cyclopentadienyl moiety of the indenyl ring and the metal, such as trihapto coordination, are also embraced by the scope of the present invention.

Preferably, in the compound of formula I wherein Ar is cyclopentadienyl, M represents Cr, Mo, Fe, Co or Ru, or a metal cation thereof. Even more preferably, M represents Cr, Fe, Co or Ru or a metal cation thereof. Most preferably, M is selected from a Group VIIIB metal or metal cation thereof. An especially preferred Group VIIIB metal (M) is Fe. Although the metal M as defined herein may be in a cationic form, preferably it carries essentially no residual charge due to coordination with L_1 and/or L_2 as defined herein.

Preferably, when n = 1 in the compound of formula I, L_1 represents cyclopentadienyl, indenyl or aryl each of which rings are optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, SR^{27} or ferrocenyl (by which is meant the cyclopentadienyl, indenyl or aryl ring which L_1 may represent is bonded directly to the cyclopentadienyl ring of the metallocenyl group). More preferably, if the cyclopentadienyl, indenyl or aryl ring which L_1 may represent is substituted it is preferably substituted with one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$ where R^{19}, R^{20}, R^{21}, R^{22}, R^{23} and R^{24} each independently represent hydrogen or C_1-C_6 alkyl.

Preferably, when n = 1, L_1 represents cyclopentadienyl, indenyl, phenyl or naphthyl optionally substituted as defined herein. Preferably, the cyclopentadienyl, indenyl, phenyl or naphthyl groups are unsubstituted. More preferably, L_1 represents cyclopentadienyl, indenyl or phenyl, each of which rings are unsubstituted. Most preferably, L_1 represents unsubstituted cyclopentadienyl.

In a particularly preferred embodiment of the present invention, in a compound of formula I, n = 1, L_1 is as defined herein and m = 0.

Alternatively, when n is equal to zero and m is not equal to zero in a compound of formula I, L_2 represents one or more ligands each of which are independently selected from lower alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$. More preferably, L_2 represents one or more ligands each of which are independently selected from C_1 to C_4 alkyl, halo, particularly chloro, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, wherein R^{43} to R^{48} are independently selected from hydrogen, C_1 to C_6 alkyl or aryl, such as phenyl.

In a particularly preferred alternative embodiment of the present invention, in a compound of formula I, n = 0, L_2 is as defined herein and m = 3 or 4, particularly 3.

M represents a metal selected from Cr, Mo, Fe, Co or Ru or a metal cation thereof;

L_1 represents cyclopentadienyl, indenyl, naphthyl or phenyl, each of which rings may be optionally substituted by one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$, $NR^{23}R^{24}$;

L_2 represents one or more ligands each of which ligands are independently selected from C_1-C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$;

n = 0 or 1;
and m = 0 to 4;

provided that when n = 1 then m = 0 and when m does not equal zero then n = 0.

Further preferred compounds of formula I include those wherein:

M represents iron or a cation thereof;

L_1 represents cyclopentadienyl, indenyl or phenyl group, each of which groups are optionally substituted by one or more substituents selected from C_1-C_6 alkyl, halo, cyano, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)R^{22}$;

L_2 represents one or more ligands each of which are independently selected from C_1-C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1-C_6 alkyl or phenyl;

n = 0 or 1; and m = 0 to 4.

Still further preferred compounds of formula I include those wherein:

L_1 represents unsubstituted cyclopentadienyl, indenyl or phenyl, particularly unsubstituted cyclopentadienyl; and, n = 1 and m = 0.

Alternative preferred compounds of formula I include those wherein:

n = 0;

L_2 represents one or more ligands each of which are independently selected from C_1 to C_6 alkyl, halo, CO, $PR^{43}R^{44}R^{45}$ or $NR^{46}R^{47}R^{48}$, where R^{43} to R^{48} are independently selected from hydrogen, C_1-C_6 alkyl or phenyl; and m = 1 to 4, particularly 3 or 4. For example, when m=3 the three ligands which L_2 may represent include $(CO)_2$halo, $(PR^{43}R^{44}R^{45})_2$halo or $(NR^{46}R^{47}R^{48})_2$halo.

Particularly preferred combinations within this embodiment of the present invention and wherein at least one 2-phospha-adamantyl group is present include those of formula (I) wherein:-

(4) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
Q^1 and Q^2 both represent phosphorus;
K represents hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen;
D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and m = 0.

(5) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;

A and B are the same and represent $-CH_2-$;
K, D and E are the same and represent hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen;
Q^1 and Q^2 both represent phosphorus;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and m = 0.

(6) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
K represents $-CH_2-Q^3(X^5)X^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;
A and B are the same and represent $-CH_2-$;
Q^1, Q^2 and Q^3 each represent phosphorus;
D and E are the same and represent hydrogen or unsubstituted C_1-C_6 alkyl, particularly hydrogen;
M represents Fe;
n = 1 and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and m = 0.

(7) $(CR^7R^8R^9)$ and $(CR^{10}R^{11}R^{12})$ together with Q^2 to which they are attached represent 2-phospha-adamantyl;
$(CR^4R^5R^6)$ and $(CR^1R^2R^3)$ together with Q^1 to which they are attached represent 2-phospha-adamantyl;
K represents $-CH_2-Q^3(X^5)X^6$ wherein X^5 and X^6 together with Q^3 to which they are attached represents 2-phospha-adamantyl;

A_1 and A_2 are the same and represent $-CH_2-$;

Q^1, Q^2 and Q^3 each represent phosphorus;

D and E together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an unsubstituted phenyl ring;

M represents Fe;

n = 1 and L_1 represents cyclopentadienyl, particularly unsubstituted cyclopentadienyl, and m = 0.

Suitably, the process of the invention may be used to catalyse the hydroformylation of an ethylenically unsaturated compound in the presence of carbon monoxide and hydrogen, i.e. the process of the invention may catalyse the conversion of an ethylenically unsaturated compound to the corresponding aldehyde. Conveniently, the process of the invention will show an increased selectivity to the linear aldehyde product, compared to the branched aldehyde product, in comparison with similar processes but where the chlorine moiety is not present. Preferably, the ratio of linear:branched product obtained from the hydroformylation process is greater than when using comparable catalyst systems/solvents but wherein a chlorine moiety is not present, i.e. the ratio is biased towards the linear product, more preferably the linear:branched ratio is greater than 1:1, more preferably is greater than 1.25:1, even more preferably is greater than 1.5:1, yet more preferably is greater than 2:1, most preferably is greater than 3:1.

Conveniently, the process of the invention may utilise highly stable compounds under typical hydroformylation reaction conditions such that they require little or no

replenishment. Conveniently, the process of the invention may have an increased rate of the hydroformylation reaction of an ethylenically unsaturated compound compared to known processes. Conveniently, the process of the invention may promote high conversion rates of the ethylenically unsaturated compound, thereby yielding the desired product in high yield with little or no impurities. Consequently, the commercial viability of the hydroformylation process, such as the hydroformylation of an ethylenically unsaturated compound, may be increased by employing the process of the invention.

The following definitions apply to all sets of embodiments noted hereinbefore and where applicable, unless otherwise stated.

The term "Ar" or "aryl" when used herein, and unless otherwise indicated, includes five-to-ten membered, preferably six-to-ten-membered carbocyclic aromatic or pseudo aromatic groups, such as phenyl, ferrocenyl and naphthyl, preferably phenyl and naphthyl, which groups are optionally substituted with, in addition to K, D, E or Z, one or more substituents selected from aryl, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below), Het, halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below).

Suitably, when Ar or aryl is cyclopentadienyl and when D and E together with the carbon atoms of the

cyclopentadienyl ring to which they are attached form a phenyl ring, the metal M or cation thereof is attached to an indenyl ring system. In a preferred embodiment Ar represents phenyl or naphthyl, more preferably, phenyl and in either case they may be optionally substituted as set out in the previous paragraph.

The term "Het", when used herein, includes four-to-twelve-membered, preferably four-to-ten-membered ring systems, which rings contain one or more heteroatoms selected from nitrogen, oxygen, sulfur and mixtures thereof, and which rings may contain one or more double bonds or be non-aromatic, partly aromatic or wholly aromatic in character. The ring systems may be monocyclic, bicyclic or fused. Each "Het" group identified herein is optionally substituted by one or more substituents selected from halo, cyano, nitro, oxo, lower alkyl (which alkyl group may itself be optionally substituted or terminated as defined below) OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$ or $C(S)NR^{25}R^{26}$ wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl (which alkyl group itself may be optionally substituted or terminated as defined below). The term "Het" thus includes groups such as optionally substituted azetidinyl, pyrrolidinyl, imidazolyl, indolyl, furanyl, oxazolyl, isoxazolyl, oxadiazolyl, thiazolyl, thiadiazolyl, triazolyl, oxatriazolyl, thiatriazolyl, pyridazinyl, morpholinyl, pyrimidinyl, pyrazinyl, quinolinyl, isoquinolinyl, piperidinyl, pyrazolyl and piperazinyl. Substitution at Het may be at a carbon atom of the Het ring or, where appropriate, at one or more of the heteroatoms.

"Het" groups may also be in the form of an N oxide.

The term "lower alkyl" when used herein, means C_1 to C_{10} alkyl and includes methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl groups. Unless otherwise specified, alkyl groups may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be substituted or terminated by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, aryl or Het, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by one or more oxygen or sulfur atoms, or by silano or dialkylsilcon groups.

Lower alkyl groups which R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}, R^{28}, K, D, E and Z may represent and with which aryl and Het may be substituted, may, when there is a sufficient number of carbon atoms, be linear or branched, be saturated or unsaturated, be cyclic, acyclic or part cyclic/acyclic, and/or be interrupted by one or more of oxygen or sulfur atoms, or by silano or dialkylsilicon groups, and/or be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, aryl or Het wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl.

Similarly, the term "lower alkylene" which A, B and J (when present) represent in a compound of formula (I), and which R represents in a compound of formula (Ia), when

used herein, includes C_1 to C_{10} groups which can be bonded at two places on the group and is otherwise defined in the same way as "lower alkyl".

Halo groups with which the above-mentioned groups may be substituted or terminated include fluoro, chloro, bromo and iodo groups.

Where a compound of the formula (I) or (Ia) contains an alkenyl group, cis (E) and trans (Z) isomerism may also occur. The present invention includes the individual stereoisomers of the compounds of formula (I) and, where appropriate, the individual tautomeric forms thereof, together with mixtures thereof. Separation of diastereoisomers or cis and trans isomers may be achieved by conventional techniques, e.g. by fractional crystallisation, chromatography or H.P.L.C. of a stereoisomeric mixture of a compound of the formula (I) or a suitable salt or derivative thereof. An individual enantiomer of a compound of the formula (I) may also be prepared from a corresponding optically pure intermediate or by resolution, such as by H.P.L.C. of the corresponding racemate using a suitable chiral support or by fractional crystallisation of the diastereoisomeric salts formed by reaction of the corresponding racemate with a suitable optically active acid or base, as appropriate.

All stereoisomers are included within the scope of the process of the invention.

It will be appreciated by those skilled in the art that the compounds of formula (I), or compounds of formula (Ia), i.e. (b) above, may function as ligands that

coordinate with the Group VIII metal or compound thereof, i.e. (a) above, to form the compounds for use in the invention. Typically, the Group VIII metal or compound thereof, i.e. (a) above, coordinates to the one or more phosphorous, arsenic and/or antimony atoms of the compound of formula (I).

The details and embodiments which follow hereinafter apply to all sets of embodiments noted hereinbefore.

As noted hereinbefore, the present invention provides a process for the hydroformylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and hydrogen in the presence of a catalyst system and solvent as defined in the present invention.

Suitably, the hydroformylation reaction is carried out at a temperature of between 20°C and 180°C, more preferably 35°C and 165°C, yet more preferably 50°C to 150°C, even more preferably 55°C to 115°C, most preferably 60°C to 95°C, for example at about 80°C, and under a partial pressure of carbon monoxide/hydrogen in the range of 1 to 700 bar, preferably 1 to 600 bar, more preferably 1 to 300 bar, even more preferably 15 to 100 bar, yet even more preferably 20 to 45 bar, most preferably 25 to 40 bar, for example at about 30 bar.

Suitably, the ethylenically unsaturated compound may include more than one carbon-carbon double bond, wherein the double bonds are conjugated or non-conjugated.

Preferably, the ethylenically unsaturated compound has 1 to 3 carbon-carbon double bonds per molecule, particularly only 1 or 2 carbon-carbon double bonds per molecule, generally only 1 carbon-carbon double bond per molecule.

In the process according to the present invention, the carbon monoxide and hydrogen may be used either in pure form or diluted with an inert gas such as nitrogen, carbon dioxide or a noble gas such as argon.

The amount of the catalyst of the invention used in the hydroformylation process of the ethylenically unsaturated compound is not critical. Good results may be obtained when, preferably, the amount of Group VIII metal is in the range 10^{-7} to 10^{-1} moles per mole of ethylenically unsaturated compound, more preferably, 10^{-6} to 10^{-2} moles, most preferably 10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound. Preferably, the amount of bidentate compound of formula (I), or of formula (Ia), to unsaturated compound is in the range 10^{-7} to 10^{-1}, more preferably, 10^{-6} to 10^{-2}, most preferably, 10^{-5} to 10^{-2} moles per mole of ethylenically unsaturated compound.

The catalyst compounds of the present invention may act as a "heterogeneous" catalyst or a "homogeneous" catalyst.

By the term "homogeneous" catalyst we mean a catalyst, i.e. a compound of the invention, which is not supported but is simply admixed or formed in-situ with the reactants of the hydroformylation reaction (e.g. the ethylenically unsaturated compound, hydrogen and carbon monoxide), preferably in a suitable solvent as described herein.

By the term "heterogeneous" catalyst we mean a catalyst, i.e. the compound of the invention, which is carried on a support.

Thus according to a further aspect, the present invention provides a process for the hydroformylation of ethylenically unsaturated compounds as defined herein wherein the process is carried out with the catalyst comprising a support, preferably an insoluble support.

Preferably, the support comprises a polymer such as a polyolefin, polystyrene or polystyrene copolymer such as a divinylbenzene copolymer or other suitable polymers or copolymers known to those skilled in the art; a silicon derivative such as a functionalised silica, a silicone or a silicone rubber; or other porous particulate material such as for example inorganic oxides and inorganic chlorides.

Preferably the support material is porous silica which has a surface area in the range of from 10 to 700 m^2/g, a total pore volume in the range of from 0.1 to 4.0 cc/g and an average particle size in the range of from 10 to 500μm. More preferably, the surface area is in the range of from 50 to 500 m^2/g, the pore volume is in the range of from 0.5 to 2.5 cc/g and the average particle size is in the range of from 20 to 200 μm. Most desirably, the surface area is in the range of from 100 to 400 m^2/g, the pore volume is in the range of from 0.8 to 2.0 cc/g and the average particle size is in the range of from 30 to 100 μm. The average pore size of typical porous support materials is in the range of from 10 to 1000 Å. Preferably, a support material is used that has an average

pore diameter of from 50 to 500 Å, and most desirably from 75 to 350 Å. It may be particularly desirable to dehydrate the silica at a temperature of from 100°C to 800°C anywhere from 3 to 24 hours.

Suitably, the support may be flexible or rigid and the insoluble support is coated and/or impregnated with the compounds of the process of the invention by techniques well known to those skilled in the art.

Alternatively, the compounds of the process of the invention are fixed to the surface of an insoluble support, optionally via a covalent bond, and the arrangement optionally includes a bifunctional spacer molecule to space the compounds from the insoluble support.

The compounds of the invention may be fixed to the surface of the insoluble support by promoting reaction of a functional group present in the compound of formula (I), for example a substituent K, D, Z and E of the aryl moiety, or formula (Ia), with a complimentary reactive group present on or previously inserted into the support. The combination of the reactive group of the support with a complimentary substituent of the compound of the invention provides a heterogeneous catalyst where the compound of the invention and the support are linked via a linkage such as an ether, ester, amide, amine, urea, keto group.

The choice of reaction conditions to link a compound of the process of the present invention to the support depends upon the nature of the substituents(s) of the

compound and the groups of the support. For example, reagents such as carbodiimides, 1,1'-carbonyldiimidazole, and processes such as the use of mixed anhydrides, reductive amination may be employed.

According to a further aspect, the present invention provides the use of the process of the invention wherein the catalyst is attached to a support.

Particularly preferred is when the organic groups R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} when associated with their respective carbon atom form composite groups which are at least as sterically hindering as t-butyl. Steric hindrance in this context is as discussed at page 14 *et seq* of "Homogenous Transition Metal Catalysis - A Gentle Art", by C Masters, published by Chapman and Hall 1981.

These steric groups may be cyclic, part-cyclic or acyclic, preferably acyclic. When cyclic or part cyclic, the group may be substituted or unsubstituted or be saturated or unsaturated. The cyclic or part cyclic groups may contain, including the tertiary carbon atom, from C_4-C_{30}, more preferably C_6-C_{20}, most preferably C_{10}-C_{15} carbon atoms in the cyclic structure. The cyclic structure may be substituted by one or more substituents selected from halo, cyano, nitro, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, SR^{27}, $C(O)SR^{27}$, $C(S)NR^{25}R^{26}$, aryl or Het, wherein R^{19} to R^{27} each independently represent hydrogen, aryl or lower alkyl, and/or be interrupted by one or more oxygen or sulphur atoms, or by silano or dialkylsilcon groups.

In certain embodiments, as noted above, the bridging group Ar is an aryl moiety, e.g. a phenyl group, which may be optionally substituted, provided that the two phosphorus atoms are linked to adjacent carbon atoms, e.g. at the 1 and 2 positions on the phenyl group. Furthermore, the aryl moiety may be a fused polycyclic group, e.g. naphthalene, biphenylene or indene. However, preferably the aryl moiety is phenyl or napthalene, more preferably phenyl.

Examples of suitable specific but non-limiting examples of bidentate ligands are 1,2-bis-(di-tert-butylphosphinomethyl)benzene, 1,2-bis-(di-tert-pentylphosphinomethyl)benzene, 1,2-bis-(di-tert-butylphosphinomethyl)naphthalene, 1,2 bis(diadamantylphosphinomethyl)benzene, 1,2 bis(di-3,5-dimethyladamantylphosphinomethyl)benzene, 1,2 bis(di-5-tert-butyladamantaylphosphinomethyl)benzene, 1,2 bis(1-adamantyl tert-butyl-phosphinomethyl)benzene, 1,2 bis(di-1-diamantanephosphinomethyl)benzene, 1-[(diadamantylphosphinomethyl)-2-(di-tert-butylphosphinomethyl)]benzene, 1-(di-tert-butylphosphinomethyl)-2-(dicongressylphosphinomethyl)benzene, 1-(di-tert-butylphosphinomethyl)-2-(phospha-adamantylphosphinomethyl)benzene, 1-(diadamantylphosphinomethyl)-2-(phospha-adamantylphosphinomethyl)benzene, 1-(tert-butyladamantyl)-2-(di-adamantyl)-(phosphinomethyl)benzene and 1-[(P-(2,2,6,6,-tetra-methylphosphinan-4-one)phosphinomethyl)]-2-(phospha-adamantylphosphinomethyl)benzene, 1,2-bis-(ditertbutylphosphinomethyl)ferrocene, 1,2-bis-(ditertbutylphosphinomethyl)ferrocene, 1,2,3-tris-

(ditertbutylphosphinomethyl)ferrocene, 1,2-bis-(dicyclohexylphosphinomethyl)ferrocene, 1,2-bis-(di-iso-butylphosphinomethyl)ferrocene, 1,2-bis-(dicyclopentylphosphinomethyl)ferrocene, 1,2-bis-(diethylphosphinomethyl)ferrocene, 1,2-bis(di-isopropylphosphinomethyl)ferrocene, 1,2-bis-(dimethylphosphinomethyl)ferrocene, 1,2-bis-(di-(1,3,5,7-tetramethyl-6,9,10-trioxa-2-phospha-adamantylmethyl))ferrocene, 1,2-bis-α,α-(P-(2,2,6,6,-tetramethylphosphinan-4-one))dimethylferrocene, and 1,2-bis-(di-1,3,5,7-tetramethyl-6,9,10-trioxa-2-phospha-adamantylmethyl))benzene, preferably selected from bis (di-t-butyl phosphino)-o-xylene (also known as 1,2 bis (di-t-butylphosphinomethyl) benzene); 1,2 bis (diadamantylphosphinomethyl) benzene; 1,2 bis (diadamantylphosphinomethyl) naphthalene; 1,2 bis (di-t-pentylphosphino)-o-xylene (also known as 1,2 bis (di-t-pentyl-phosphinomethyl) benzene); and bis 1,2 (di-t-butyl phosphinomethyl) naphthalene. Additionally, the bidentate phosphine may be bonded to a suitable polymeric substrate via at least one of the bridging group Ar, the linking group A or the linking group B, e.g. bis (di-t-butyl phosphino)-o-xylene may be bonded via the xylene group to polystyrene to give an immobile heterogeneous catalyst.

The amount of bidentate ligand used can vary within wide limits. Preferably, the bidentate ligand is present in an amount such that the ratio of the number of moles of the bidentate ligand present to the number of moles of the Group VIII metal present is from 1 to 50, e.g. from 1 to 10, and particularly from 1 to 5, mol per mol of metal. More preferably, the mol:mol range of compounds of formula (I) or (Ia), preferably formula (I), to Group VIII metal

is in the range of 1:1 to 3:1, most preferably in the range of 1:1 to 1.25:1. Conveniently, the possibility of applying these low molar ratios is advantageous, as it avoids the use of an excess of the compound of formula (I) or (Ia), preferably formula (I), and hence minimises the consumption of these usually quite expensive compounds. Suitably, the catalysts of the process of the invention are prepared in a separate step preceding their use in-situ in the hydroformylation reaction of an ethylenically unsaturated compound.

The carbon monoxide and hydrogen may be used in the presence of other gases which are inert in the reaction. Examples of such gases include nitrogen, carbon dioxide and the noble gases such as argon.

Suitable Group VIII metals (otherwise known as Group VIIIB metals) or a compound thereof which may be combined with a compound of formula (I) include cobalt, nickel, palladium, rhodium, ruthenium and platinum. Preferably, (a) is rhodium or a compound thereof. Suitable compounds of such Group VIII metals include salts of such metals with, or compounds comprising weakly coordinated anions derived from, nitric acid; sulphuric acid; lower alkanoic (up to C_{12}) acids such as acetic acid and propionic acid; sulphonic acids such as methane sulphonic acid, chlorosulphonic acid, fluorosulphonic acid, trifluoromethane sulphonic acid, benzene sulphonic acid, naphthalene sulphonic acid, toluene sulphonic acid, e.g. p-toluene sulphonic acid, t-butyl sulphonic acid, and 2-hydroxypropane sulphonic acid; sulphonated ion exchange resins; perhalic acid such as perchloric acid; halogenated carboxylic acids such as trichloroacetic acid and

trifluoroacetic acid; orthophosphoric acid; phosphonic acids such as benzenephosphonic acid; and acids derived from interactions between Lewis acids and Broensted acids. A further alternative includes halo salts. Other sources which may provide suitable anions include the optionally halogenated tetraphenyl borate derivatives, e.g. perfluorotetraphenyl borate. Moreover, metal complexes, particularly those with labile ligands, may be used. Of course, the process of the invention requires a catalyst system obtainable by combining a Group VIII metal or a compound thereof and a bidentate phosphine, with the presence of a chlorine moiety in at least one of the Group VIII metal compound or the solvent, and therefore should the solvent not contain a chlorine moiety, the Group VIII metal compound must contain a chlorine moiety, and the foregoing is to be read accordingly. Of course, should the chlorine moiety be present in the solvent, then the moiety can be present in any part of the solvent system, e.g. wherein the solvent system may comprise a solvent and, for example, a chlorine moiety source, preferably the chlorine moiety is present within the chemical structure of the solvent molecules themselves, e.g. in chlorohydrocarbon solvents, chlorofluorocarbon solvents, and the like.

The catalyst system of the present invention is preferably constituted in the liquid phase which may be formed by one or more of the reactants or by the use of a suitable solvent. Clearly, in the former case, the references to solvent in the present invention should be construed accordingly and the chlorine moiety must, in such cases, be present in the Group VIII metal compound.

The choice of solvent is not critical, aside from the fact that according to the invention, it must comprise a chlorine moiety if the Group VIII metal compound does not. Naturally, the solvent chosen should not be detrimental to either the catalyst system, reactants or products. Moreover, the solvent can be a mixture of reactants, such as the ethylenically unsaturated compound, the product and/or any by-products, and the higher-boiling products of secondary reactions thereof, e.g. aldol condensation products. Moreover, more than one solvent can be present, e.g. a mixture of solvents.

Suitable solvents, when present, include saturated hydrocarbons such as kerosene, mineral oil or cyclohexane, ethers such as diphenyl ether, methyl phenyl ether, diethylether, diisopropylether, tetrahydrofuran or a polyglycol, ketones such as acetone, methyl ethyl ketone, methyl butyl ketone and cyclohexanone, nitriles such as methylglutaronitrile, valeronitrile, and benzonitrile, aromatics, including halo variants, such as toluene, benzene and xylene, esters such as methylacetate, methylvalerate and caprolactone, dimethylformamide, and sulfones such as tetramethylenesulfone, and variants of any of the aforesaid comprising at least one chlorine moiety.

Other suitable solvents include aromatic compounds such as toluene (as noted above), hydrocarbons or mixtures of hydrocarbons. It is also possible to use water, and alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol. Variants of the aforesaid comprising at least one chlorine moiety are also suitable.

As noted hereinbefore, a chlorine moiety is present in at least one of the Group VIII metal compound or solvent of the process of the invention. Thus, suitably, the Group VIII metal compound is as defined hereinbefore and comprising a chlorine moiety. Specific examples of suitable Group VIII compounds include rhodium complexes (both those with and those without at least one chlorine moiety) and are such as $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$ (wherein "Cod" represents "1,5-cyclooctadiene"), $RhCl_3.xH_2O$, $[Rh(CO)_2(acac)]_2$ (wherein "acac" represents "acetylacetonate"), $[Rh(acetate)_2]_2$, $[RhCl(Norbornadiene)]_2$, $Rh_2(OAc)_4$, $[RhCl(Cyclooctene)_2]_2$, Chloro(1,5-hexadiene)-rhodium(I)dimer, Bis(1,5-cyclooctadiene)-rhodium(I)tetraflouroborate hydrate, μ-dichlorotetraethylene-dirhodium, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, (1,5-cyclooctadiene)(2,4-pentanedionato)rhodium(I), (bicyclo[2,2,1]hepta-2-5-diene)(2,4-pentanedionato)rhodium(I), rhodium(III)acetylacetonate, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, more especially $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$, $RhCl_3.xH_2O$, $[Rh(CO)_2(acac)]_2$, $[Rh(acetate)_2]_2$ $[RhCl(Norbornadiene)]_2$ $[RhCl(Cyclooctene)_2]_2$, Chloro(1,5-hexadiene)-rhodium(I)dimer, most especially $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$, $RhCl_3.xH_2O$, $[Rh(CO)_2(acac)]_2$, $[Rh(acetate)_2]_2$. Thus, where the rhodium complexes are to comprise at least one chlorine moiety, suitable complexes include $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$, $RhCl_3.xH_2O$, $[RhCl(Norborn-adiene)]_2$, $[RhCl(Cyclooctene)_2]_2$, Chloro(1,5-hexadiene)-rhodium(I)dimer, μ-dichlorotetraethylene-dirhodium, (bicyclo[2,2,1]hepta-2-5-diene)chlororhodium(I)dimer, more especially $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$, $RhCl_3.xH_2O$, $[RhCl(Norbornadiene)]_2$,

$[RhCl(Cyclooctene)_2]_2$, Chloro(1,5-hexadiene)-rhodium(I)dimer, most especially $[RhCl(CO)_2]_2$, $[RhCl(Cod)_2]_2$, $RhCl_3.xH_2O$. Moreover, suitably, the solvent of the process of the invention is as defined hereinbefore and comprising a chlorine moiety. Specific examples of such solvents comprising at least one chloro moiety include dichloromethane, chlorobenzene, o-dichlorobenzene, m-chlorobenzene, carbon tetrachloride, trichloroethanes, dichloroethanes, chlorofluorocarbons (CFC's), tetrachloroethanes, tetrachloroethene, more especially dichloromethane. Even more preferably, both the Group VIII metal compound and the solvent contain a chlorine moiety.

The product of the reaction may be separated from the other components by any suitable means. However, it is an advantage of the present process that significantly fewer by-products are formed thereby reducing the need for further purification after the initial separation of the product as may be evidenced by the generally significantly higher selectivity and linearity. A further advantage is that the other components which contain the catalyst system may be recycled and/or reused in further reactions with minimal supplementation of fresh catalyst.

Preferably, the hydroformylation is carried out at a temperature of between 20°C and 180°C, more preferably 35°C and 165°C, yet more preferably 50°C to 150°C, even more preferably 55°C to 115°C, most preferably 60°C to 95°C, for example at about 80°C. Advantageously, the hydroformylation can be carried out at moderate temperatures. It is particularly advantageous to be able

to carry out the hydroformylation reaction at above room temperature.

Suitably, the hydroformylation is carried out at the partial pressure of the reaction gas mixture at the chosen reaction temperature. Generally, the partial pressure is in the range of 1 to 700 bar, preferably 1 to 600 bar, more preferably 1 to 300 bar, even more preferably 15 to 100 bar, yet even more preferably 20 to 45 bar, most preferably 25 to 40 bar, for example at about 30 bar. However, the partial pressure may be varied from these ranges depending on the activity of the hydroformylation catalyst employed. In the case of catalyst systems of the present invention, for example, reaction would also proceed in a low-pressure region, for example in the range 1 to 100 bar.

The reaction may be carried out on any ethylenically unsaturated compound including ethylene although there is no linearity advantage as such with ethylene. Preferably, the reaction is therefore suitable for C_3-C_{20} ethylenically unsaturated compounds, more preferably, C_3-C_{18}, most preferably C_3-C_{12} compounds.

The process may be carried out on ethylenically unsaturated compounds having 2 or more carbon atoms such as C_2-C_{20} atoms or C_3-C_{20} atoms or C_4-C_{20} atoms. The alternative upper range of carbon atoms in such compounds may be taken as C_{18} or C_{15} or C_{12} in increasing order of preference. The alternative lower range of carbon atoms in any of the aforesaid ranges of ethylenically unsaturated compounds may be C_3, C_4, C_5 or C_6. The ethylenically unsaturated compound is, preferably, an

alkene having 1, 2 or 3 or more carbon-carbon double bonds per molecule.

Any such alkene can be substituted or non-substituted. Suitable substituents include C_{1-8} alkyl and C_{1-22} aryl groups. Unless otherwise specified, the ethylenically unsaturated compound may, when there are sufficient number of carbon atoms, be linear or branched, be substituted, be cyclic, acyclic or part cyclic/acyclic, and/or be optionally substituted or terminated by one or more substituents selected from lower alkyl, aryl, alkylaryl, Het, alkylHet, halo, OR^{19}, $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, NO_2, CN, SR^{27} wherein R^{19} to R^{27} each independently represent hydrogen or lower alkyl. Olefins thus substituted include styrene and alkyl esters of unsaturated carboxylic acids, such as methacrylate. Suitably, the ethylenically unsaturated compound may exhibit cis (E) and trans (Z) isomerism.

Examples of suitable ethylenically unsaturated compounds may be independently selected from ethene, propene, 1-butene, 2-butene, isobutene, 1-pentene, 2-pentene, 3-pentene and branched isomers thereof, 1-hexene and its isomers, 1-heptene and its isomers, 1-octene and its isomers, 1-nonene and its isomers, 1-decene and its isomers, the C_{11}-C_{20} alkenes and their known isomers, 3-pentenenitrile, methyl-3-penteneoate, 1,3 butadiene, 1,3-pentadiene, 1,3 hexadiene, 1,3 cyclohexadiene, 2,4-leptadiene, and 2-methyl 1,3 butadiene. Preferably, the ethylenically unsaturated compound is a C_2-C_{20} alkene, more preferably a C_3-C_{20} alkene with a carbon-carbon double bond in the 1-position, most preferably a C_3-C_{12} or C_6-C_{12} alkene with a carbon-carbon double bond in the 1-position.

The use of stabilising compounds with the catalyst system may also be beneficial in improving recovery of metal which has been lost from the catalyst system. When the catalyst system is utilized in a liquid reaction medium such stabilizing compounds may assist recovery of the Group VIIIB metal.

Preferably, therefore, the catalyst system includes in a liquid reaction medium a polymeric dispersant dissolved in a liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the Group VIII metal or metal compound of the catalyst system within the liquid carrier.

The liquid reaction medium may be a solvent for the reaction or may comprise one or more of the reactants or reaction products themselves. The reactants and reaction products in liquid form may be miscible with or dissolved in a solvent or liquid diluent.

The polymeric dispersant is soluble in the liquid reaction medium, but should not significantly increase the viscosity of the reaction medium in a way which would be detrimental to reaction kinetics or heat transfer. The solubility of the dispersant in the liquid medium under the reaction conditions of temperature and pressure should not be so great as to deter significantly the adsorption of the dispersant molecules onto the metal particles.

The polymeric dispersant is capable of stabilising a colloidal suspension of particles of said Group VIII metal or metal compound within the liquid reaction medium such

that the metal particles formed as a result of catalyst degradation are held in suspension in the liquid reaction medium and are discharged from the reactor along with the liquid for reclamation and optionally for re-use in making further quantities of catalyst. The metal particles are normally of colloidal dimensions, e.g. in the range 5 - 100 nm average particle size although larger particles may form in some cases. Portions of the polymeric dispersant are adsorbed onto the surface of the metal particles whilst the remainder of the dispersant molecules remain at least partially solvated by the liquid reaction medium and in this way the dispersed Group VIII metal particles are stabilised against settling on the walls of the reactor or in reactor dead spaces and against forming agglomerates of metal particles which may grow by collision of particles and eventually coagulate. Some agglomeration of particles may occur even in the presence of a suitable dispersant but when the dispersant type and concentration is optimised then such agglomeration should be at a relatively low level and the agglomerates may form only loosely so that they may be broken up and the particles redispersed by agitation.

The polymeric dispersant may include homopolymers or copolymers including polymers such as graft copolymers and star polymers.

Preferably, the polymeric dispersant has sufficiently acidic or basic functionality to substantially stabilise the colloidal suspension of said Group VIII metal or metal compound.

By substantially stabilise is meant that the precipitation of the Group VIII metal from the solution phase is substantially avoided.

Particularly preferred dispersants for this purpose include acidic or basic polymers including carboxylic acids, sulphonic acids, amines and amides such as polyacrylates or heterocycle, particularly nitrogen heterocycle, substituted polyvinyl polymers such as polyvinyl pyrrolidone or copolymers of the aforesaid.

Examples of such polymeric dispersants may be selected from polyvinylpyrrolidone, polyacrylamide, polyacrylonitrile, polyethylenimine, polyglycine, polyacrylic acid, polymethacrylic acid, poly(3-hydroxybutyricacid), poly-L-leucine, poly-L-methionine, poly-L-proline, poly-L-serine, poly-L-tyrosine, poly(vinylbenzenesulphonic acid) and poly(vinylsulphonic acid).

Preferably, the polymeric dispersant incorporates acidic or basic moieties either pendant or within the polymer backbone. Preferably, the acidic moieties have a dissociation constant (pK_a) of less than 6.0, more preferably, less than 5.0, most preferably less than 4.5. Preferably, the basic moieties have a base dissociation constant (pK_b) being of less than 6.0, more preferably less than 5.0 and most preferably less than 4.5, pK_a and pK_b being measured in dilute aqueous solution at 25°C.

Suitable polymeric dispersants, in addition to being soluble in the reaction medium at reaction conditions, contain at least one acidic or basic moiety, either within

the polymer backbone or as a pendant group. We have found that polymers incorporating acid and amide moieties such as polyvinylpyrollidone (PVP) and polyacrylates such as polyacrylic acid (PAA) are particularly suitable. The molecular weight of the polymer which is suitable for use in the invention depends upon the nature of the reaction medium and the solubility of the polymer therein. We have found that normally the average molecular weight is less than 100,000. Preferably, the average molecular weight is in the range 1,000 - 200,000, more preferably, 5,000 - 100,000, most preferably, 10,000 - 40,000 e.g. Mw is preferably in the range 10,000 - 80,000, more preferably 20,000 - 60,000 when PVP is used and of the order of 1,000 - 10,000 in the case of PAA.

The effective concentration of the dispersant within the reaction medium should be determined for each reaction/catalyst system which is to be used.

The dispersed Group VIII metal may be recovered from the liquid stream removed from the reactor e.g. by filtration and then either disposed of or processed for re-use as a catalyst or other applications. In a continuous process the liquid stream may be circulated through an external heat-exchanger and in such cases it may be convenient to locate filters for the palladium particles in these circulation apparatus.

Preferably, the polymer:metal mass ratio in g/g is between 1:1 and 1000:1, more preferably, between 1:1 and 400:1, most preferably, between 1:1 and 200:1. Preferably, the polymer:metal mass ratio in g/g is up to 1000, more preferably, up to 400, most preferably, up to 200.

In a further aspect the present invention provides a catalyst system, preferably wherein said system is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said system, the catalyst system obtainable by combining:

a) a Group VIII metal compound as described or defined hereinbefore; and
b) a bidentate phosphine as described or defined hereinbefore,

and wherein the catalyst system is characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

In a yet further aspect the present invention provides a hydroformylation reaction catalyst system for the catalysis of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of said system, the catalyst system obtainable by combining:

a) a Group VIII metal compound as described or defined hereinbefore; and
b) a bidentate phosphine as described or defined hereinbefore,

and wherein the catalyst system is characterised in that a chlorine moiety is present in at least said Group VIII metal compound.

In a still further aspect the present invention provides a reaction medium comprising a catalyst system and a solvent, preferably wherein said medium is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said system and said solvent, wherein said solvent is as described or defined hereinbefore, the catalyst system obtainable by combining:

a) a metal of Group VIII or a compound thereof as described or defined hereinbefore; and
b) a bidentate phosphine as described or defined hereinbefore,

and wherein the reaction medium is characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent, including the possibility of being present in both.

In a still yet further aspect the present invention provides a hydroformylation reaction medium, wherein said medium comprises a catalyst system and a solvent, preferably wherein said system is for use in a process for the hydroformylation of ethylenically unsaturated compounds and which process comprises reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said system and said solvent, wherein said solvent is as described or defined hereinbefore, the catalyst system obtainable by combining:

a) a metal of Group VIII or a compound thereof as described or defined hereinbefore; and
b) a bidentate phosphine as described or defined hereinbefore,

and wherein the reaction medium is characterised in that a chlorine moiety is present in at least one of the said Group VIII metal compound or said solvent, including the possibility of being present in both.

In a still yet further aspect of the present invention there is provided the use of a catalyst system as defined or described hereinbefore for the hydroformylation of ethylenically unsaturated compounds, said use comprising the step of reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said catalyst system.

In a still yet further aspect of the present invention there is provided the use of a reaction medium as defined or described hereinbefore for the hydroformylation of ethylenically unsaturated compounds, said use comprising the step of reacting said ethylenically unsaturated compound with carbon monoxide and hydrogen, in the presence of said reaction medium.

In a still further aspect of the present invention there is provided a process for preparing a catalyst system or a reaction medium as defined or described hereinbefore, comprising combining (a) a metal of Group VIII or a compound thereof as described or defined hereinbefore, and (b) a bidentate phosphine as described or defined hereinbefore.

Features and embodiments of the first aspect of the invention are equally applicable to any or all of the various aspects of the present invention as set out herein, unless such features/embodiments are incompatible with the particular aspect, or are mutually exclusive.

The following non-limiting and purely illustrative examples further illustrate the present invention.

All syntheses were carried out in a vacuum-argon Schlenk line using dried and degassed Schlenk glassware.

1-octene and 1-hexene (both from Aldrich) were purified by distillation and degassed by bubbling with argon. Toluene was dried by distillation from sodium diphenyl ketal. THF (tetrahydrofuran) was dried by distillation with sodium and benzophenone. DCM (dichloromethane) was dried by distillation with calcium hydride.

$[RhCl(CO)_2]_2$, $Rh_2(OAc)_4$, and $RhCl_3.xH_2O$ (Strem) were stored in a glove box due to their air-sensitive nature. 1,2-bis (di-tertbutylphosphinomethyl)benzene was also stored and handled in a glove box due to its air-sensitive nature.

1,2-bis(di-tertbutylphosphinomethyl)benzene is available from Strem Chemicals (Catalog 19 No. 15-0072, CAS No. 121954-50-5) or can, as in these examples, be prepared as per example 18 of WO-A-99/47528, PCT/GB99/00797, details of the preparation being incorporated by reference thereto.

The preparation details of 1,2-bis-(diadamantylphosphinomethyl)benzene and other adamantyl-based ligands are given in the Applicant's published application, WO-A-04/014552, PCT/GB03/003419, herein incorporated by reference, particularly for such preparation details.

The preparation details of 1,2-bis-(di-t-butylphosphinomethyl)ferrocene and other ferrocene-based ligands are given in the Applicant's published application, WO-A-04/024322, PCT/GB03/003936, herein incorporated by reference, particularly for such preparation details.

The catalytic solutions were made up as follows.

For catalytic systems having $[RhCl(CO)_2]_2$ as rhodium precursor, 9mg (0.023mmol) of $[RhCl(CO)_2]_2$ and 20mg (0.046mmol) of 1,2-bis(di-tertbutylphosphinomethyl)benzene were added to a Schlenk tube in a glove box. The corresponding solvent (typically 10ml) was then added with a syringe. When all the solids were dissolved, 1-octene or 1-hexene (2ml), the substrate for hydroformylation, was added to the solution.

The autoclaves used for these examples were 250ml hastelloy autoclaves. After being dried in an oven, the autoclave was flushed three times with argon. Once it was degassed, the solution was transferred via canula. Then it was pressured with 30bar of synthesis gas and heated to 80°C for 3hrs, after which it was cooled in air and then vented. The solutions obtained were analysed with GC-MS.

The catalytic systems in which either $Rh_2(OAc)_4$ or $RhCl_3$ were used as rhodium precursors, were prepared following the same procedure as that outlined above.

The percentage conversion is an expression of the amount of substrate converted by the reaction.

The selectivity is a measure of the selectivity to the particular hydroformylated product.

l:b is a representation of the linear:branched ratio of the hydroformylated products.

Example 1

Hydroformylation of 1-hexene: Chlorine moiety present in rhodium precursor

9.0 mg (0.00383mol/litre) of $[RhCl(CO)_2]_2$ was added to 18 mg (0.00383mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0 ml (16.0mmol) of 1-hexene was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of $CO:H_2$ at a pressure of 30bar.

It was found that after 3hrs under these conditions, there was 100% conversion of 1-hexene to the aldehyde product, with 84% selectivity to linear heptanal over the branched product, an l:b ratio of 5.25:1.

Comparative Example 1

Hydroformylation of 1-hexene: Chlorine moiety not present

10 mg (0.00383mol/litre) of $[Rh(OAc)_2]_2$ was added to 40 mg (0.00846mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0ml (16.0mmol) of 1-hexene was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of $CO:H_2$ at a pressure of 30bar.

It was found that after 3hrs under these conditions, there was 100% conversion of 1-hexene to the aldehyde product, with 55% selectivity to linear heptanal over the branched product, an l:b ratio of only 1.22:1.

Comparative Example 1 and Example 1 clearly show the increase in selectivity towards the linear product over the branched product, from the hydroformylation of 1-hexene, when chlorine moiety is present in the rhodium compound precursor to the catalyst system compared with when the chlorine moiety is not present.

Example 2

Hydroformylation of allyl alcohol: Chlorine moiety present in rhodium precursor

9.0 mg (0.00383mol/litre) of $[RhCl(Cod)_2]_2$ was added to 18.0 mg (0.00383mol/litre) of the bidentate phosphine ligand, 1,2-bis(di-tertbutylphosphinomethyl)benzene. 10ml of toluene was then added to the mixture. 2.0 ml (29.0mmol) of allyl alcohol was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of $CO:H_2$ at a pressure of 30bar, and in the presence of 0.072mmol of NaOAc.

It was found that after 3hrs under these conditions, there was 86.6% conversion of allyl alcohol, with 73.8% selectivity to hydroxytetrahydrofuran, 12.9% to hydroxymethyl-propionaldehyde. These two products were then hydrogenated to give, respectively, 1,4-butanediol and 2-methyl-1,3-propanediol. The l:b ratio in this case was 5.72:1.

Example 3

Hydroformylation of allyl alcohol: Chlorine moiety present in solvent

Example 2 was repeated but in this case, the rhodium compound was $[Rh(OAc)_2]_2$ and the solvent used was dichloromethane.

In this case, there was 100% conversion of allyl alcohol, with 75% selectivity to hydroxytetrahydrofuran, 17% hydroxymethylpropionaldehyde, giving hydrogenated products in the l:b ratio 4.41:1.

Examples 2 and 3 show the relatively high selectivity towards the linear as opposed to the branched product, from the hydroformylation of allyl alcohol, when chlorine moiety is present in the rhodium compound precursor to the catalyst system (Example 2) or in the solvent (Example 3).

Example 4

Hydroformylation of 1-octene: Chlorine moiety present in solvent

5.0 mg (0.0016mol/litre) of $[Rh(acac)(CO)_2]_2$ was added to 18.0 mg (0.00383mol/litre) of the biphosphine ligand, 1,2-

bis(di-tertbutylphosphinomethyl)benzene. 10ml of dichloromethane was then added to the mixture. 2.5 ml (16mmol) of 1-octene was then added and hydroformylation was performed for 3hrs by the addition, at 80°C, of a 1:1 mixture of $CO:H_2$ at a pressure of 30bar.

It was found that after 3hrs under these conditions, there was 29% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an l:b ratio of 4:1.

Example 5

Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor and in solvent

Details were as in Example 4 above, except 9.0 mg (0.00383mol/litre) of $[RhCl(CO)_2]_2$ was used as the rhodium precursor.

Once again, it was found that there was 29% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an l:b ratio of 4:1.

Example 6

Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor

Details were as in Example 5 above, except 10ml of OctMiMTfN, 1-octyl-3-methylimidazolium bis-trifluoromethylsulphonamide, a non-chlorine containing solvent, was used as the solvent.

In this case, it was found that there was 10% conversion to the aldehyde product, with 80% selectivity to linear nonanal over the branched product, an l:b ratio of 4:1.

Example 7
Hydroformylation of 1-octene: Chlorine moiety present in rhodium precursor

Details were as in Example 5 above, except 10ml of toluene was used as the solvent.

In this case, it was found that there was 11% conversion to the aldehyde product, with 100% selectivity to linear nonanal.

Comparative Example 2
Hydroformylation of 1-octene: Chlorine moiety not present

Details were as in Example 4 above, except 10ml of toluene was used as the solvent.

In this case, it was found that there was 89% conversion to the aldehyde product, with only 50% selectivity to linear nonanal, an l:b ratio of 1:1.

Examples 4-7 clearly show the increase in selectivity towards the linear product over the branched product, from the hydroformylation of 1-octene, when chlorine moiety is present in the solvent (Example 4), the rhodium precursor (Examples 6 and 7), or both the solvent and the rhodium precursor (Example 5), compared to Comparative Example 2, where no chlorine moiety is present, either in the rhodium precursor or in the solvent.

Although a few preferred embodiments have been shown and described, it will be appreciated by those skilled in the art that various changes and modifications might be made without departing from the scope of the invention, as defined in the appended claims.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any

accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.